THE RELATION BETWEEN THE DEGREE OF FINENESS OF PYRETHRUM POWDER PRODUCED BY DIFFERENT PERIODS OF GRINDING TO TOXICITY TO INSECTS AND TO DETERIORATION BY LIGHT AND AIR*

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INTRODUCTION

The increasing demand for insecticides non-poisonous to human kind has made it imperative that the efficiency of the present materials, such as pyrethrum powder, be increased to the utmost in an effort to replace the poisonous materials now in use.

The writer found there was little information on the effect of particle size of pyrethrum powder on toxicity, and on its deterioration by light and air. Methods of protecting pyrethrum powder from deterioration have only been touched upon by investigators. Work was, therefore, undertaken towards improving the efficiency of pyrethrum powder when applied as a dust or in water suspension.

The purpose of the work reported in this paper is to establish definite relationships:

(1) between the fineness of pyrethrum powder and its toxicity to insects,

(2) between the fineness of pyrethrum powder and its rate of deterioration when exposed to light and air, and

(3) between the fineness of pyrethrum powder and the degree of protection afforded by certain pigments and anti-oxidants from deterioration by light and air.

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REVIEW OF LITERATURE

A. Effect of Fineness of Pyrethrum Powder on Toxicity to Insects

Only slight mention has been made in the literature of the relationship between fineness of pyrethrum powder and toxicity. Work on improving the physical properties of dust materials has consisted in the main of altering the carrier used rather than in varying the fineness of the ground flowers.

Richardson (12) states that coarse powder (15 to 45 mesh) gives an extractive efficiency of about 80 per cent, whereas a fine 200 mesh powder gives a significantly higher extractive efficiency. Gnadinger and Corl (6) showed that the achenes contained 92.4 per cent of the total pyrethrins. The achenes are not broken up until a fineness of 200 mesh is reached.

B. Effect of Fineness of Pyrethrum Powder on Rate of Decomposition by Light and Air

Hartzell and Wilcoxin (7) found that commercially ground pyrethrum powder exposed to sunlight, ultra-violet light, and heat resulted in a loss of pyrethrins determined chemically, and a loss of toxicity to aphids. Tattersfield (15) reports that both artificially prepared dusts and ground pyrethrum flowers lose their insecticidal activity on exposure to light and air. He states: "Both light and air play an important part in the process of inactivation, as samples of Kieselguhr-pyrethrum or talc-pyrethrum dusts stored in closed vessels in the dark or exposed to the air in the dark are relatively stable; also samples exposed to light in an atmosphere of CO_2, nitrogen, or in vacua lose little of their toxicity under the same conditions of illumination; samples exposed in oxygen, however, rapidly lose their activity."

C. Protection of Pyrethrum Powder from Loss of Toxicity by Addition of Pigments or Anti-Oxidants

A great deal of work has been done with anti-oxidants in relation to the stabilization of oils, fats, vitamins, etc. No better explanation for the action of anti-oxidants has been advanced than the theory of antagonistic peroxides given by Moureu and Dufraisse (10). They suppose the peroxide $A(O)_2$, oxidizes the anti-oxygen B, with the formation of a peroxide B(O), while it is itself transformed into another peroxide A(O). The two peroxides A(O) and B(O) are antagonistic, and mutually destroy each other, with regeneration of the three original molecules A, B, O_2.

$$A + O_2 \rightarrow A(O)_2;\ A(O)_2 + B \rightarrow A(O) + B(O)$$
$$A(O) + B(O) \rightarrow A + B + O_2$$

Another hypothesis, is that of a direct auto-oxidation of the anti-oxygen; in this case we have the following cycle:

$$A + O_2 \rightarrow A(O)_2;\ B + O_2 \rightarrow B(O)_2$$
$$A(O)_2 + B(O)_2 \rightarrow A + B + 2O_2$$

It is noted that A, O_2 have been taken from the state of *activated molecules* at the moment of their combination, and returned to the mixture in an inactivated state.

A great amount of experimental data has been accumulated supporting this theory. Tattersfield (15) reports that "the incorporation of anti-oxidants with talc-pyrethrum and Kieselguhr-pyrethrum dusts retards loss of activity due to exposure to light and air." Some of the phenolic compounds tested gave a considerable measure of protection.

Jones, *et al.* (9) used lampblack with rotenone (equal parts) and secured a measurable protection from decomposition upon exposure to light and air. Neither bentonite nor the substances naturally occurring with rotenone in powdered derris root protected rotenone from decomposition. Hamilton and Ben Amotz (unpublished data), working on the theory that certain colored pigments might protect pyrethrum from light, ran tests on a large number of pigments. It soon became evident that the protection was not due to the color of the pigments. The writer continued this work under Dr. Hamilton's direction. It was found that those pigments which have a high index of reflection or absorption of the wave lengths of light injurious to the toxic principles of derris or pyrethrum powder and which also had good covering properties were most efficient in protecting the powder from deterioration. While this field of study has not been exhausted, the best protecting agent found when this work was started was titanium dioxide, and it was used in the tests reported herewith.

EXPERIMENTAL METHODS

Preparation of Pyrethrum Flowers for Testing

A quantity of high quality Japanese flowers ground for percolation was procured from McCormick & Company, Inc., of Baltimore, Maryland. In order to secure a material which was of fairly uniform size for a starting point these flowers were ground for five hours in a ball mill, then screened through a 50 mesh wire. The residue from this screening was ground in the ball mill for another five hours and screened as before. The residue from the second screening was discarded. When a sufficient quantity of flowers had been prepared in this manner they were thoroughly mixed. Analyses were run on the flowers before and after grinding.

Analyses of Pyrethrum Flowers

	Before Grinding	*After Grinding*
Pyrethrins I and II (Gnadinger and Corl copper reduction method)	0.91 per cent	1.11 per cent
Non-volatile petroleum ether extract	4.37 per cent	4.50 per cent
Moisture	5.61 per cent	6.28 per cent
Total ash	6.39 per cent	6.72 per cent
Acid insoluble ash	0.48 per cent	0.52 per cent

The quality of the flowers was raised by removing the chaff in screening. This screened material was used in all tests reported in this paper.

If sieves were used to separate the powder into samples of different degrees of fineness, the finer samples would contain a higher percentage of pyrethrins due to the fact that the seed achenes would be in those samples. Gnadinger and Corl (6) found the seed achenes to contain 92.4 per cent. of the total pyrethrins in the flowers.

Upon consideration of the above facts, it was decided to divide the ground flowers into a number of equal portions and regrind these samples in the ball mill for different lengths of time.

Photomicrographs were made of these different grinds when spread on plates in a film approaching one particle in thickness. These pictures (shown in plates X and XI under two magnifications) show the difference in particle size produced by the different lengths of grinding. The appearance of the clear, sharp-edged particles should be noted for another series of the same grinds coated with titanium dioxide was also made. The distinguishing feature of the second series is the white fringed appearance of the particles.

Preparation of Protected Powders

Fifteen per cent of TiO_2 was mixed roughly with the ground pyrethrum. The mixture was then put through a corn mill twice, so as to give a uniform coating of the particles. This mill was so constructed that the shearing motion of the plates could be adjusted to give very little grinding of the pyrethrum flowers. Microscopic examination showed a very uniform coating of the particles after two passages through the mill (see plates XI and XII).

In preparing the pyrethrum powder protected with an antioxidant, a mixture consisting of 50 per cent tannic acid crystals dissolved in methyl cellosolve (ethylene glycol-mono-methyl ether) was prepared and allowed to stand overnight. Ten per cent of this 50–50 mixture was added to the ground pyrethrum and worked in thoroughly with a mortar and pestle. This gave a material consisting of 90 per cent pyrethrum flowers, 5.0 per cent tannic acid and 5.0 per cent methyl cellosolve. In commercial practice, this material could be diluted with acetone or some other solvent and sprayed into the dust.

Methods and Equipment Used in Exposing Pyrethrum to Light

The source of light was an Uviarc Mercury Vapor outfit designed for operation on alternating current. The voltage was adjustable by resistances, and was run on a line carrying 118 volts. The lamp current was 4.8 amperes and the wattage 450.

It is simple to operate, and requires no complicated radiating fins to control its temperature. It provides a standard light source of great intensity. An exposure of 1 hour to this light is equivalent in its effect on pyrethrum powder to a full day of bright June sunlight. In other words, it is approximately 12 times as effective as the sun at this time of year in producing loss of toxicity in pyrethrum powder.

The table upon which exposures were to be made was inclined at an angle of 3° above the horizontal so as to parallel the light source which operates at that angle. The distance from the mercury arc to the table top was 20 inches. Material was not placed under the lamp for testing until the intensity of the light was constant, *i.e.*, until the mercury was completely vaporized in the arc and the liquid mercury driven back into the cathode end of the tube.

Eastman Kodak ($3\frac{1}{2} \times 4''$) thin cover glasses for lantern slides were coated with the dusts for exposure. It was difficult to secure an even coat of the pyrethrum one particle in thickness on the clean glass inasmuch as the powders consisted of particles of different sizes. It was finally found that the best method was to coat the slides with a very thin, even layer of Nujol, and then to pour the dust material carefully over the slide. The excess dust was jarred off. Even after considerable practice about 15 to 20 per cent of the plates had to be discarded.

The thin layers of dust were examined by direct and reflected light and beneath an Ultrapac microscope to make certain that the dust was evenly applied and of the required thickness. Weighings were made on all slides used in the first two series of tests and those slides which were not within 10 per cent of the mean were discarded. Only a few slides had to be discarded. The average weights of the dust films were 30 mg.

As a further check on the methods used, 40 slides were prepared without special attention to equality in thickness of films. The ten heaviest slides and the ten lightest slides were selected, exposed to the light and tested on aphis. No appreciable effect on the kill was secured though the difference between the weights of the two series was 20 per cent of the total weight.

Tests were also run against *Aphis rumicis* and against mosquito larvæ to find out whether the oil film had any effect on toxicity. No appreciable difference could be detected between the dry materials and those which were dusted on an oiled slide.

METHODS OF BIOLOGICAL TESTING USED

In testing the pyrethrum flowers of different finenesses three methods were used. First, the time of 50 per cent paralysis of mosquito larvæ was determined; second, the mortality of *Aphis rumicis* was determined when the ground flowers were applied in water suspension; and third, the mortality to *Aphis rumicis* was determined when the ground flowers were used as a dust.

The first tests were conducted on mosquito larvæ. These larvæ were identified as the species *Culex quinquefasciatus* Say by Mr. Carl Ilg of this station. The egg boats were sent by mail from the U. S. Bureau of Entomology Station at Orlando, Florida. The method of rearing the larvae and conducting the tests was essentially the same as that used by Campbell (2).

The material to be tested was weighed out and diluted to the required volume and immediately poured over fourth instar larvæ from which all the water had been drawn off. All materials were tested simultaneously on larvæ from the same batch, and duplicates were run on each material. The larvæ were removed as soon as they showed definite sign of paralysis. In this way the time of 50 per cent paralysis was obtained.

The spray tests on *Aphis rumicis* were conducted as follows: 300 to 400 insects were used in each test. The dilutions were made immediately before spraying, and one-tenth of one per cent soap was added to give wetting without adding appreciable toxicity. The insects were sprayed under uniform pressure until the plants were thoroughly wet. Counts were made after 24 hours and dead, moribund, and alive were recorded.

The dust tests on *Aphis rumicis* were conducted as follows. Plants were selected whose leaves had just started to bend over. A modification of the apparatus used by Campbell and Filmer (1) for coating leaves with arsenicals was developed and proved very satisfactory for securing an even coating of dust on the insects and leaves. A charge of 0.4 g. was blown into the bell jar and the dust allowed to settle for 7 minutes. Practically all the dust could be delivered in this manner. Those aphis which had fallen from the plant were carefully transferred to the paper with a camel's hair brush. Counts were made as above after 24 hours. The charge used was equivalent to 30 pounds per acre in a cloud one foot deep.

PRESENTATION OF DATA

As was pointed out in the introduction, the purpose of this investigation was to establish three relationships:— (1) between the fineness of pyrethrum powder and its toxicity to insects, (2) between the fineness of pyrethrum powder and its rate of deterioration when exposed to light and air, and (3) between the fineness of pyrethrum powder and the degree of protection from deterioration by light and air afforded by certain pigments and anti-oxidants.

Three different methods of biological testing were used in order to arrive at conclusions concerning the above relationships. The data presented are averages of 5 or more individual tests. It is not feasible to present all of these individual tests in this paper, but it was necessary to run them in order to insure sound conclusions.

The first method used was the determination of the 50 per cent paralytic point for mosquito larvæ. The fineness of the pyrethrum was varied only by increasing the time of grinding in the ball mill. The data in table 1 show the time of 50 per cent paralysis, for unexposed powder of different fineness, for exposed powder of different finenesses, and for exposed powder of different finenesses to which had been added a protective pigment.

The mortality to *Aphis rumicis* was determined when the materials were applied in water suspension. The data in table II are the average of 5 tests. Each test consisted of 300 to 400 insects. The data show the per cent kill for unexposed powder of different fineness, for exposed powder of different finenesses, and for exposed powder of different finenesses to which has been added either a protective pigment or an anti-oxidant.

The mortality to *Aphis rumicis* was also determined when the materials were applied as a dust. The data in Table III are the average of 5 tests. Each test consisted of 300 to 400 insects.

TABLE I

TESTS ON MOSQUITO LARVÆ TO DETERMINE THE EFFECT OF PARTICLE SIZE OF PYRETHRUM POWDER ON RATE OF PARALYSIS OF THE LARVÆ, RATE OF DECOMPOSITION OF THE POWDER BY LIGHT AND AIR, AND DEGREE OF PROTECTION FROM DECOMPOSITION SECURED BY COATING THE POWDER WITH TITANIUM DIOXIDE

Treatment and Dilution	*Hours Reground*				
	2.5	*5.0*	*10.0*	*20.0*	*30.0*
	Time of 50% Paralysis in Minutes				
Series A					
(a) Unexposed—no protectant ($1–60 \times 10^6$)	277.0	72.0	35.5	15.0	10.5
(b) " " " ($1–20 \times 10^6$	10.5	8.0	6.0	3.0	1.75
(c) 1.5 hours Exposure—no protectant ($1–20 \times 10^6$)	17.0	57.5	399.0	*	*
(d) 1.5 hours Exposure—15% TiO_2 ($1–20 \times 10^6$)	13.0	12.75	10.0	8.5	7.0
Series B					
(a) Unexposed—no protectant ($1–20 \times 10^6$)	12.0	10.5	8.0	5.25	3.5
(b) 2.0 hours Exposure—no protectant ($1–20 \times 10^6$)	*	*	*	*	*
(c) 2.0 hours Exposure—15% TiO_2 ($1–20 \times 10^6$)	26.5	29.9	23.7	27.5	35.0
Series C					
(a) Unexposed—no protectant ($1–30 \times 10^6$)	145.0	41.0	22.0	10.5	7.0
(b) 3.0 hours Exposure—no protectant ($1–30 \times 10^6$)	*	*	*	*	*
(c) 3.0 hours Exposure—15% TiO_2 ($1–30 \times 10^6$)	*	*	*	*	*

* = no 50% paralytic point reached within 24 hours.

TABLE II

SUMMARY OF SPRAY TESTS ON *Aphis rumicis* TO DETERMINE THE EFFECT OF PARTICLE SIZE OF PYRETHRUM POWDER ON MORTALITY TO APHIS, RATE OF DECOMPOSITION OF THE POWDER BY LIGHT AND AIR, AND DEGREE OF PROTECTION FROM DECOMPOSITION SECURED BY ADDING TITANIUM DIOXIDE OR TANNIC ACID

Treatment, Dilution and Exposure	*Hours Reground*				
	2.5	*5.0*	*10.0*	*20.0*	*30.0*
	% Kill of Aphis rumicis				
Unexposed—no protectant (1–30,000 + 0.1% soap)					
Series 1	43%	44%	61%	63%	71%
Series 2	66%	69%	76%	78%	82%
Series 3	53%	55%	59%	62%	64%
Series 4	63%	64%	68%	70%	77%
Exposed—no protectant (1–30,000 + 0.1% soap)					
Series 1 = 1.5 hours	39%	32%	21%	22%	20%
Series 2 = 1.5 hours	33%	30%	28%	24%	26%
Series 3 = 1.5 hours	38%	30%	26%	23%	20%
Series 4 = 3.0 hours	31%	28%	28%	23%	22%
Exposed—15% Titanium Dioxide (1–30,000 + 0.1% soap)					
Series 2 = 1.5 hours	66%	58%	55%	66%	71%
Exposed—5% Tannic Acid (1–30,000 + 0.1% soap)					
Series 3 = 1.5 hours	51%	53%	61%	62%	63%
Series 4 = 3.0 hours	48%	58%	51%	36%	37%

The data show the per cent kill for unexposed powder of different finenesses, for exposed powder of different finenesses, and for exposed powder of different fineness to which has been added either a protective pigment or an anti-oxidant.

DISCUSSION AND INTERPRETATION OF RESULTS

Part I. The Effect of Particle Size of Pyrethrum Powder on Toxicity to Insects

The data show that there is a very remarkable decrease in the time required for paralysis of 50 per cent of *Culex quinque-*

TABLE III

SUMMARY OF DUST TESTS ON *Aphis rumicis* TO DETERMINE THE EFFECT OF PARTICLE SIZE OF PYRETHRUM POWDER ON MORTALITY TO APHIS, RATE OF DECOMPOSITION OF THE POWDER BY LIGHT AND AIR, AND DEGREE OF PROTECTION FROM DECOMPOSITION SECURED BY ADDING TITANIUM DIOXIDE OR TANNIC ACID

Treatment and Exposure	*Hours Reground*				
	2.5	*5.0*	*10.0*	*20.0*	*30.0*
	% Kill of Aphis rumicis				
Unexposed—no protectant					
Series 1	73%	76%	80%	83%	84%
Series 2	68%	74%	79%	79%	86%
Series 3	56%	59%	62%	67%	68%
Exposed—no protectant					
Series 1 = 1 hour	38%	32%	30%	23%	29%
Series 2 = 1.5 hours	22%	19%	15%	15%	14%
Series 3 = 1.5 hours	42%	27%	24%	21%	21%
Exposed—15% Titanium Dioxide					
Series 1 = 1 hour	72%	82%	83%	84%	85%
Series 2 = 1.5 hours	67%	62%	66%	69%	74%
Exposed—5% Tannic acid					
Series 3 = 1.5 hours	53%	54%	54%	55%	58%

fasciatus larvæ as the particle size of the powder decreases. Examination of the data (Table I, Series A, Test (a)) shows that the finest material gave 50 per cent paralysis in 10.5 minutes whereas the coarsest material tested gave the same result in 277.0 minutes. Another test (Series C, Test (a)) shows a range of 7.0 minutes to 145.0 minutes between the finest and coarsest materials.

The explanation for this relationship follows. Pyrethrins are only very slightly soluble in water, but they are extracted by water and form a colloidal suspension. Therefore, the greater the surface of the pyrethrum powder exposed to the water the more rapid is the dispersion of the pyrethrins. The mosquito larva is very susceptible to pyrethrins even in extremely low concentrations, and hence, is a very sensitive indicator of the rapidity of this extraction.

The variation in mortality to *Aphis rumicis* secured with the water suspensions of the unexposed pyrethrum of different finenesses was not as marked as the paralytic effect on mosquito larvæ. This is because the aphid is harder to kill and not affected by such small quantities of pyrethrins as the mosquito larva.

However, the kills obtained with the coarsest material and the finest material were as follows 43 per cent and 71 per cent, 66 per cent and 82 per cent, 63 per cent and 77 per cent. (See the unexposed materials Table II). These differences of 14 to 28 per cent are significant, especially when one considers that they are averages of 5 tests. Individual tests showed a range of as much as 35 per cent between the 2.5 and 30 hour grinds.

Since the water suspensions of the dusts were made up just previous to spraying, the same explanation applies here as was given for the quicker paralytic effects on mosquito larvæ. That is, the plant cells were broken up small enough in the longer periods of grinding to make the dispersion of pyrethrins more rapid.

When the pyrethrum powder of different finenesses was tested as a dust, the variation in mortality was of the same order as that found when the materials were applied in water suspension. The kills obtained with the coarsest and finest materials were as follows:— 73 per cent and 84 per cent, 68 and 86 per cent, 56 per cent and 68 per cent. (See unexposed material Table III.) As was pointed out above, these differences are significant as each figure is the average of 5 tests.

In explanation of these results with dusts, it is necessary to discuss briefly the method by which pyrethrum dust is believed to kill insects. Ginsburg (3) has shown that the toxic principles of pyrethrum are not volatile. Shafer (13) traced the entrance of dust materials into the spiracles by adding dye to the powder. The material did not penetrate very far into the trachea. Thus, the pyrethrins must be taken into the insect's body in solution. The solution is probably effected by the moisture and body exudate occurring on the insect's integument. The pyrethrins then gain entrance in solution through the integument or sensory pores on the insect's body. Hartzell and Wilcoxin (8) showed that concentrated oleoresin of pyrethrins entered the insect's body through the integument. Tischler (unpublished data) showed that pyrethrum and derris dust affected the insect by passing directly through the integment.

Part II. The Effect of Particle Size of Pyrethrum Powder on the Loss of Toxicity When Exposed to Light and Air

The data show that, when pyrethrum powder is exposed to light from the mercury vapor lamp in air, the finer the particle size the more rapid is the decomposition produced. Examination of the data (Table I, Series A, Test (c)) shows that the time of 50 per cent paralysis was 17.0 minutes for the coarsest material after 1.5 hours exposure whereas with the two finest grinds the 50 per cent point had not been reached in 24 hours. With the unexposed material in this same series (Test (b)) the coarsest material gave 50 per cent paralysis in 10.5 minutes and the finest material gave 50 per cent paralysis in 1.75 minutes. An exposure of 2.0 hours completely destroyed the toxicity of all the materials tested, both coarse and fine.

Spray and dust tests on *Aphis rumicis* also showed the same result. That is, the finer particles were less toxic after exposure than the coarser materials. The data in Table II (Spray Tests—1.5 hours exposure) show kills ranging from 31–39 per cent in four series of tests with the coarsest material, while with the finest material in these same tests the kills ranged from 20–26 per cent. The data in Table III (Dust Tests—1.5 hours exposure) show kills ranging from 22–42 per cent for the coarsest material and 14 to 21 per cent for the finest material. When one considers the fact that before exposure the finer materials gave much higher kills than the coarser materials, these results are further accentuated. Thus, in two tests when the coarsest materials showed a drop of 4 to 14 per cent the finest materials showed a drop of from 47 to 55 per cent.

This toxicity data on aphis together with the paralytic tests on mosquito larvæ seem to show that with limited exposure the pyrethrins are protected somewhat from decomposition by light in the coarser material because they are in the unbroken cell.

Part III. The Effect of Treating Pyrethrum Powder with Titanium Dioxide or Tannic Acid in Retarding Loss of Toxicity Upon Exposure to Light and Air

The decomposition of pyrethrins by light from the mercury vapor lamp in air can be retarded for a limited time by the addition of titanium dioxide or of tannic acid. Unprotected material exposed for the same length of time loses 60–70 per cent of its toxicity. Even with the protectant added, the finer particles lose their toxicity more rapidly than the coarser ones, but the ratio is not as great as with the unprotected material.

The data in Table I (see Series A, (b, c, d)), show that pyrethrum powder coated with titanium dioxide lost very little of its toxicity when exposed to light for 1.5 hours. The untreated pyrethrum powder lost its toxicity and required a much longer time to reach a paralytic point of 50 per cent. In the 20 and 30 hour grinds it had not been reached at the end of 24 hours.

The pyrethrum powder not coated with TiO_2 and not exposed to light produced 50 per cent paralysis of mosquito larvæ in 12 minutes for the coarser to 3.5 minutes for the finer powder (see Series B). The powder not coated with TiO_2 but exposed for 2 hours to the light did not give 50 per cent paralysis with any of the materials at the end of 24 hours. On the other hand, powders ground for the same lengths of time, coated with 15 per cent TiO_2 and exposed to light for 2 hours gave 50 per cent paralysis in 26.5 minutes for the coarser grinds to 35 minutes for the finer grinds.

When the materials were exposed for 3 hours (See Series C), toxicity was destroyed in both the untreated material and in the material coated with TiO_2. This shows that there is a gradual loss of toxicity in pyrethrum powder treated with TiO_2, and that the protective action does extend for more than 3 hours exposure to the mercury vapor lamp.

Spray tests on *Aphis rumicis* (Table II, Series 2) show that with 1.5 hours exposure the lowering in kill ranged from 34–54 per cent with the untreated materials whereas, with the materials coated with TiO_2 it ranged from 1 to 20 per cent with an average lowering of 10 per cent.

When tannic acid was used as a protectant, no lowering in kill was observed after an exposure of 1.5 hours while the unprotected material showed a drop of 14 to 46 per cent. With a 3 hour exposure the protection afforded by the tannic acid was beginning to decrease rapidly. It has been found by Moureu and Dufraisse (10) and other workers that a material which acts as an anti-oxidant may upon continued exposure or changed conditions act as a pro-oxidant and actually hasten the reaction which is had been retarding. This appears to be the case in the above experiments. When titanium dioxide was used, a gradual loss in toxicity was observed probably because the particles were not entirely coated with the pigment or because the pigment did not exclude all the injurious wave lengths of light.

Dust tests gave a duplication of the results of the spray tests on aphis. With an exposure of 1 hour there was a range in kill of 23–38 per cent for the unprotected material, and a range of 72 to 85 per cent for the material coated with TiO_2. The unexposed material ranged from 73–85 per cent. Thus, for this period of exposure the TiO_2 had prevented a decomposition which otherwise would have amounted to 60 per cent. (See Table III.)

With 1.5 hours exposure, the range in kill for the unprotected material was 13 to 21 per cent, and 62 to 74 per cent for the material coated with TiO_2. The unexposed material gave kills ranging from 67 to 86 per cent. This shows a lowering of 5 to 10 per cent in the material protected with TiO_2 against a lowering of 46 to 72 per cent in the unprotected material. Material protected with tannic acid showed only 4 to 10 per cent drop in kill after an exposure of 1.5 hours (see Table III).

SUMMARY

The following general conclusions may be drawn from the data presented:

(1) The finer the pyrethrum powder is ground the more rapid is the rate of paralysis of mosquito larvæ and the speed of kill of *Aphis rumicis.* The tests on aphids were conducted both as sprays and dusts with duplication of results. It appears that in each case the determining factor is the surface area of the ground particles exposed to the extracting medium.

(2) Secondly, paralytic and mortality tests conducted as above showed that the finer the pyrethrum is ground the more rapid is

the deterioration of the toxic principles upon exposure to light. Thus, the increase in surface area exposed to the light causes a quicker destruction of the pyrethrins.

(3) It would appear at first sight that the advantage of quicker kill secured by finer grinding is more than offset by the greater destruction of the toxic principles upon exposure to light in air. Data is presented, however, which shows that the deterioration of pyrethrum by light can be prevented for a limited time by either tannic acid, an anti-oxidant, or titanium dioxide, a pigment which reflects or absorbs the injurious wave lengths of light. The degree of protection secured does not vary with the different finenesses of pyrethrum powder.

(4) Even when the protectants are present, the pyrethrum powder begins to lose toxicity after a certain length of exposure. The material containing titanium dioxide holds its toxicity slightly longer than that containing tannic acid.

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PLATE X

Figure X. Pyrethrum flowers ground for percolation (×52.0).
Figure 1a. Pyrethrum powder reground 2.5 hours (×52.0).
Figure 1b. Pyrethrum powder reground 2.5 hours (×176.0).
Figure 2a. Pyrethrum powder reground 5.0 hours (×52.0).
Figure 2b. Pyrethrum powder reground 5.0 hours (×176.0).
Figure 3a. Pyrethrum powder reground 10.0 hours (×52.0).
Figure 3b. Pyrethrum powder reground 10.0 hours (×176.0).

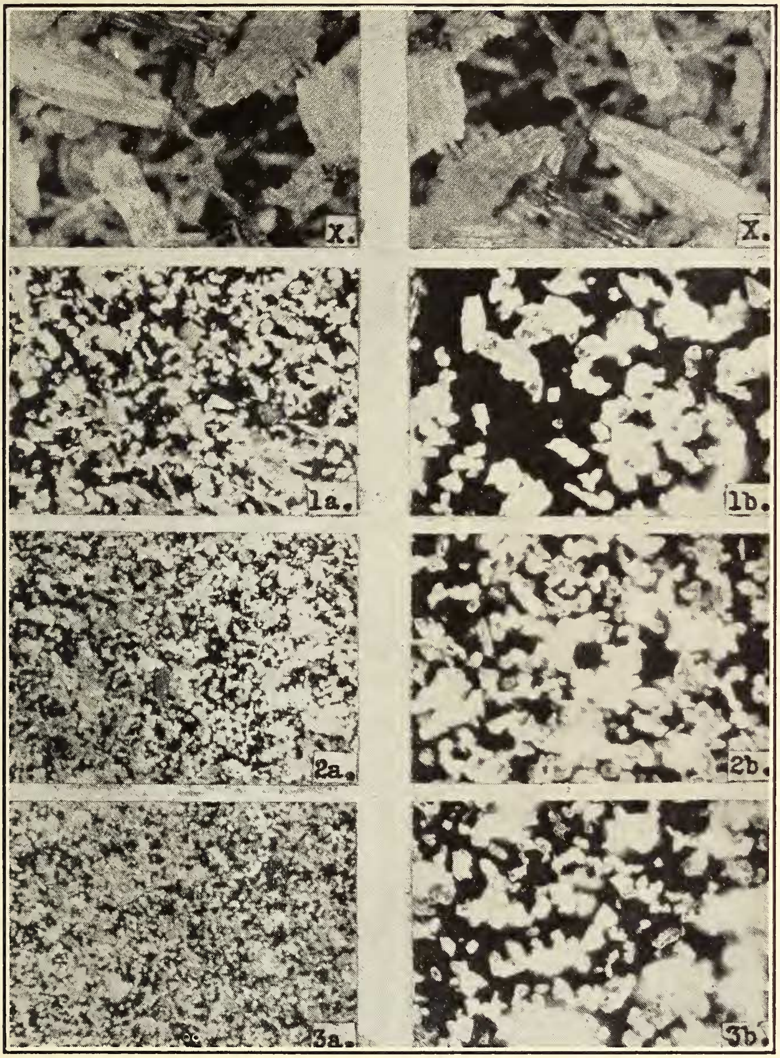

X.
X.
1a.
1b.
2a.
2b.
3a.
3b.

PLATE XI

Figure 4a. Pyrethrum powder reground 20.0 hours (×52.0).
Figure 4b. Pyrethrum powder reground 20.0 hours (×176.0).
Figure 5a. Pyrethrum powder reground 30.0 hours (×52.0).
Figure 5b. Pyrethrum powder reground 30.0 hours (×176.0).
Figure 6a. Pyrethrum powder reground 2.5 hours coated with TiO_2 (×52.0). For same material without pigment see Figure 1a, Plate X.
Figure 6b. Pyrethrum powder reground 2.5 hours coated with TiO_2 (×176.0). For same material without pigment see Figure 1b, Plate X.
Figure 7a. Pyrethrum powder reground 5.0 hours coated with TiO_2 (×52.0). For same material without pigment see Figure 2a, Plate X.
Figure 7b. Pyrethrum powder reground 5.0 hours coated with TiO_2 (×176.0). For same material without pigment see Figure 2b, Plate X.

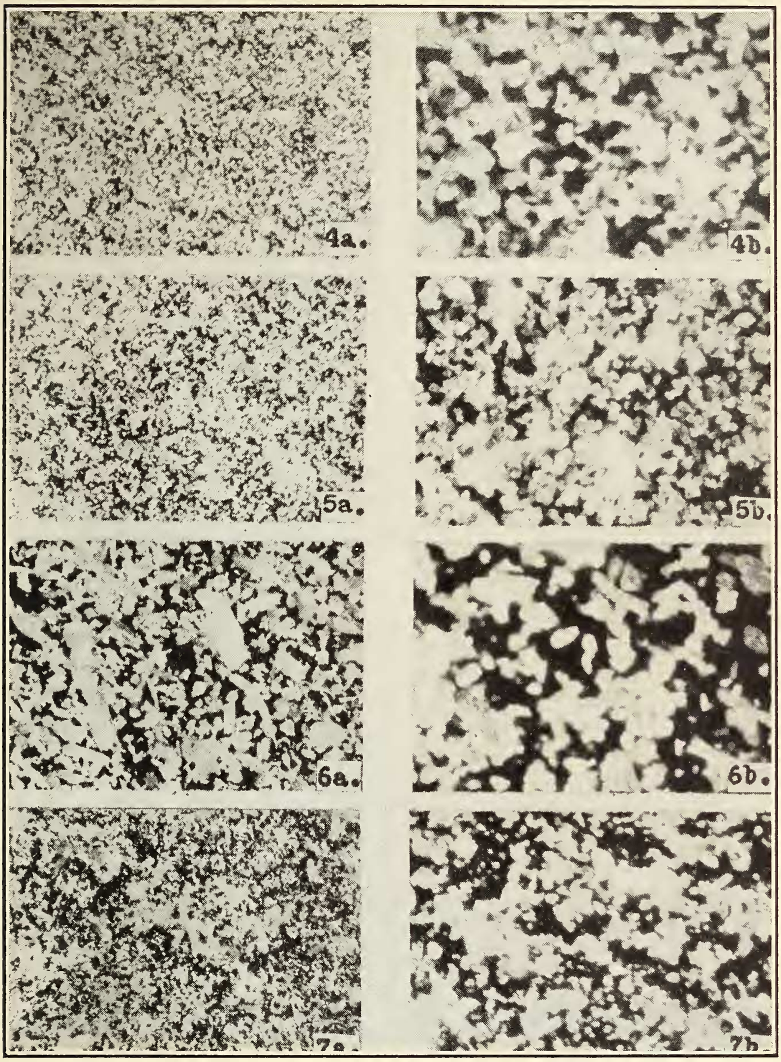

4a.
4b.
5a.
5b.
6a.
6b.
7a.
7b.

PLATE XII

Figure 8a. Pyrethrum powder reground 10.0 hours coated with TiO_2 (×52.0). For same material without pigment see Figure 3a, Plate X.

Figure 8b. Pyrethrum powder reground 10.0 hours coated wtih TiO_2 (×176.0). For same material without pigment see Figure 3b, Plate X.

Figure 9a. Pyrethrum powder reground 20.0 hours coated with TiO_2 (×52.0). For same material without pigment see Figure 4a, Plate XI.

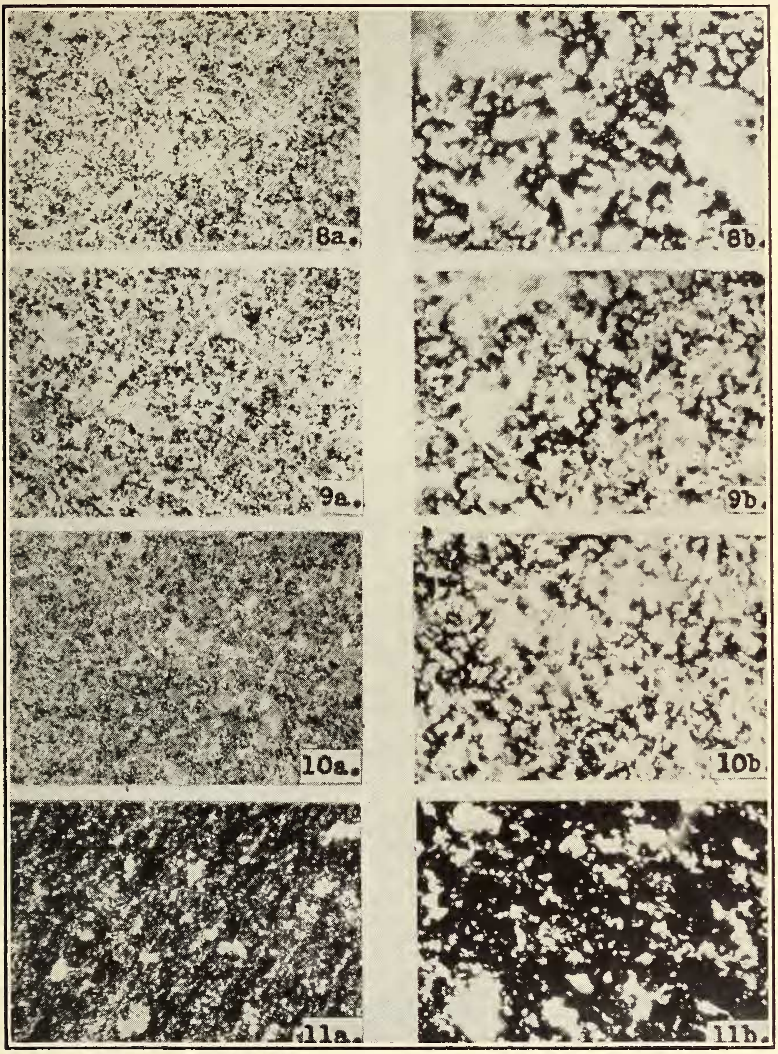
Figure 9b. Pyrethrum powder reground 20.0 hours coated with TiO_2 (×176.0). For same material without pigment see Figure 4b, Plate XI.

Figure 10a. Pyrethrum powder reground 30.0 hours coated with TiO_2 (×52.0). For same material without pigment see Figure 5a, Plate XI.

Figure 10b. Pyrethrum powder reground 30.0 hours coated with TiO_2 (×176.0). For same material without pigment see Figure 5b, Plate XI.

Figure 11a. Titanium dioxide pigment (×52.0).

Figure 11b. Titanium dioxide pigment (×176.0).


8a.
8b.
9a.
9b.
10a.
10b
11a.
11b.